DOUBLE RESONANCE MODULATED MICROWAVE SPECTROSCOPY

G. W. Flynn*, O. Stiefvater, and R. Volpicelli

Research Systems Inc., 236 Grove St., Lexington, Mass.

I. Introduction

A large number of molecular systems which have measurable vapor pressures at dry ice or room temperature can be studied by microwave spectroscopy. In general it is necessary that these molecules possess a permanent dipole moment (usually greater than 0.1 Debye) and have rotational states with energy level spacings which correspond to frequencies in the microwave spectral range (8-40 GHz, or 0.29 - 1.33 cm^{-1}). Most molecules have been studied in the microwave range with a "standard" Hughes and Wilson Stark-modulated spectrometer.[1] In this sytem the molecule is placed in a waveguide cell at a pressure of 10-100 μ of Hg. Microwave radiation is passed through the cell and absorbed by the molecular system at frequencies corresponding to the energy level separations of certain pairs of rotational states. It is important to realize that this resonance absorption for levels i, j with $E_i - E_j = h\nu_{ij}$ (where E_i, E_j are the energies of states i,j and h is Planck's constant) involves only two levels(we neglect here possible overlap between two or more transitions and degeneracies). In order to enhance the sensitivity for detection of the absorbed microwave radiation, a large electric field (0-2000V/cm) is applied to the gas in the cell. The interaction of the molecular dipole moment with this field causes a shift in the rotational energy level spacings and a consequent shift in the microwave absorption frequencies. The large electric field is modulated in square wave fashion, usually at 100KHz, and hence the absorption of radiation is also modulated at the same frequency and can be detected with a phase sensitive detector.

The standard Stark spectrometer can be characterized as a single resonance device because it involves the resonant absorption for only a single line (one pair of rotational energy levels). It is also possible to simultaneously irradiate a gaseous system with two microwave radiation fields with frequencies corresponding to two different rotational resonances of the molecule. Such experiments have been pursued by several authors[2-4] in Stark modulated spectrometers where the basic detection scheme still involves the molecular Stark effect. However, when two microwave fields are applied to a gaseous sample, it is possible to eliminate the standard high voltage Stark modulated cell by modulating one of the microwave fields instead.[5,6] This last spectroscopic scheme has been characterized as double resonance modulated microwave spectroscopy and constitutes the main concern of this abstract.

II. Theoretical Considerations

The theoretical treatment used here assumes that the resonance lines are pressure broadened. The average lifetime of a rotational state is taken as the mean time between collisions. Only three rotational energy levels, 1, 2, 3 with energies $E_1 < E_2 < E_3$ are considered. The transitions $1 \rightarrow 2$ and $2 \rightarrow 3$ are assumed to be allowed with dipole moment matrix elements μ_{12} and μ_{23} and resonance frequencies $\omega_0' = 2\pi\nu_{12}$, $\omega_0 = 2\pi\nu_{23}$. Two radiation fields are allowed to impinge upon the gaseous sample, a strong field $E' = E_0' \cos\omega' t$ and a weak field $E = E_0 \cos\omega t$ with ω' near ω_0' and ω near ω_0 but $|\omega' - \omega| > |$GHz. (See figure 1a) τ is defined to be the average collision lifetime for the states 1, 2, 3 and n_1, n_2, n_3 are the number of molecules per cm^3 in states 1, 2, 3 for the gas at thermal equilibrium. It is useful to define the parameters $x = (\mu_{23}E_0)/(2\hbar)$ and $y = (\mu_{12}E_0')/(2\hbar)$.

All double resonance experiments of interest in this work are such that the transitions induced by the fields E and E' occur between pairs of rotational levels which have one common energy level (i.e. level 2 for $1 \rightarrow 2$, $2 \rightarrow 3$). The power in the radiation field E' is taken to be sufficient to "saturate the transition $1 \rightarrow 2$. This is equivalent to saying $|y|^2\tau^2 >> |$. The power in E however is assumed to be so low that the $2 \rightarrow 3$ transition is not "saturated" ($|x|^2\tau^2 << |$). Physically, saturation corresponds to a situation where the rate of transitions induced by a radiation field between two levels is such that the population difference between the levels involved in the transition is no longer described by the thermal equilibrium value.

The main features of microwave modulated double resonance spectroscopy are: (1) the strong (high power) field E' is used to modulate the gaseous molecular sample by interacting with the energy levels 1 and 2; (2) the modulation produced by E' causes small but readily detectable changes in the absorption of radiation from the weak field E by transitions between the levels 2 and 3; (3) the signal detected consists essentially of the power absorbed from the weak field E; (4) the strong field E' is blocked from the crystal receiver and is never detected.

Javan[7] in a classic paper has given a mathematical description of a three level system interacting with two radiation fields. The theory is directly applicable to microwave double resonance but the mathematical details are too complex to present here. Therefore only a very qualitative and intuitive description will be given in what follows.

For weak radiation fields it is generally true that only single quantum transitions can take place in a molecular system due to absorption of radiation. Thus a molecule can absorb a photon from field E and go from state 2 to state 3. In the presence of a very large field such as E' at the $1 \rightarrow 2$ molecular resonance frequency and a weaker field E at the $2 \rightarrow 3$ molecular resonance frequency, it is possible for a molecule in state 1 to simultaneously absorb a photon from both E' and E and make a transition to state 3 directly via a double quantum transition. Such transitions are allowed due to the strong quantum mechanical mixing of states 1 and 2 by E'. In a double resonance experiment the power absorbed from E consists of two terms: (1) power absorbed by molecules making the usual single quantum transition $2 \rightarrow 3$; (2) power absorbed by molecules making a two quantum jump from $1 \rightarrow 3$.

In a microwave modulated double resonance spectrometer the field E' is square wave modulated between the values $E' = E'_0 \cos \omega' t$ $\omega'_1 = \omega'_0$ and $|\omega'_2 - \omega'_0| = 20 MHz$. In such a situation, for power levels in the E' field of the order of one watt or less, $E' = E'_0 \cos \omega'_2 t$ generally has only a small effect on the molecular system because ω'_2 is so far from ω'_0. Thus it is possible to take $E' = 0$ for half the square wave cycle without introducing much error.[8] If phase sensitive detection locked to the modulation frequency of E' is used to detect the power absorbed from E, the power absorbed from E during the $E' = 0$ half of the modulation cycle will be essentially identical to an ordinary single resonance absorption. The power absorbed during the $E' = E_0 \cos \omega_0 t$ half cycle will have the double

resonance shape predicted by Javan's theory.

III. Pressure Dependence and Intensity of Double Resonance Signal

In the case where E' is only an 0.1 watt field at the J=0-1 resonance frequency the lineshape for the OCS J=1-2 transition will have the appearance shown in figure 1b. As the pressure increases the signal "height" S will decrease and the "line width" will increase in a somewhat complex manner.[9]

Using a computer to simulate line shapes in OCS, the "line intensity" S for the $J=1 \rightarrow 2$ transition with an 0.1 Watt pump field at the J=0-1 resonance frequency has been determined as a function of pressure. These calculations correspond to the line shape shown in figure 1b. A table of S versus pressure and τ is given in Table 1 below for this case.

Table 1

S (arbitrary units)	P (μ of Hg)	τ* (sec x 10^{+6})
3.15	2	12.40
3.19	10	2.48
3.03	20	1.24
1.05	100	0.248
0.27	200	0.124

*$\Delta \nu = 12$ MHz/mm, full width at half height, see ref. 10.

At low pressure, for E' a 1 Watt pump field, it is possible to compare the theoretical intensity S_1 (Figure 1c) with that which can be obtained from a single resonance Stark modulated spectrometer. When the S_1 and S_2 lines are well resolved, S_1 is very similar to a single resonance absorption and it might be expected that the intensity is the same as that for the equivalent Stark modulated line. This is not true normally and the theoretical intensity is expected to be less in general for the double resonance spectrometer. The problem which arises here has to do with the effect of the pumping radiation on various molecular M states (M is the projection of the total angular momentum J on a space fixed axis). This effect becomes small as higher J values are studied and is treated in detail elsewhere.[9] There are also some practical technical problems to be considered in comparing Stark and double resonance spectrometers. Because of the absence of a Stark plate in the double resonance system, the double resonance wave guide cell can easily be made about five times as long as the corresponding Stark cell thus enhancing the signal intensity by a substantial amount. Finally, there are some subtle intensity effects in a double resonance spectrometer which arise from the rate of relaxation of the rotational states and may lead to some enhancement in signal intensity over the Stark case. These effects should be negligible in most cases.[9]

IV. Experimental Results

Several molecules have been investigated in the present experiments using a double resonance modulated spectrometer similar to that of reference 6. Only the results for propionaldehyde are considered here. For this molecule the $2_{11} \rightarrow 3_{12}$ ($\omega_o/2\pi = 33,347$ MHz) transition was observed while the $2_{02} \rightarrow 2_{11}$ ($\omega_o'/2\pi = 13474.9$ MHz) transition was pumped. The line shape corresponded to that shown in Figure 1b. Figure 2 is a plot of the signal height S (see Figure 1b) as a function of pressure for pure propionaldehyde.

It can be seen that the signal height begins to fall off drastically for pressures in excess of about 25μ of Hg. This behavior is qualitatively similar to that predicted using computer simulated line shapes for the molecule OCS (see Table 1).

The reason for the initial rise in the signal height in the pressure range 0-20 μ of Hg is readily understood by the following considerations. For pressures below about 10 μ of Hg the linewidth of the signal is not determined by collision processes and hence the theoretical discussion presented earlier does not apply to this region. Before pressure broadening sets in, the linewidth will generally be a constant (determined by the modulation frequency, temperature, and cell dimensions) and the line intensity will increase directly as the density of the sample. This is similar to the situation observed in a Stark spectrometer except that for the Stark case the maximum signal height is independent of pressure in the pressure broadened range. For the double resonance case the line intensity drops in the pressure broadened range because of incomplete modulation.

For gas samples which are mixtures of several components (all or only one of which have a microwave spectrum) curves similar to that shown in Figure 2 are observed for a given component. The peak of the signal generally occurs at a different pressure than that for the pure sample due to the difference in collision cross sections for the various constituents of the sample. It is worth noting that the double resonance technique serves as an unambiguous identification method for a molecule in the presence of many other molecules. This is because the observation of a double resonance signal for a given microwave pump and observation frequency requires that the sample have a resonance at each of these respective frequencies and that these resonances must have a <u>common</u> energy level. That such a series of circumstances might arise for more than one molecule is highly unlikely.

V. Conclusions

1. At moderate or low pressures (about 20μ of Hg) it is expected that a microwave modulated double resonance spectrometer will have a better signal to noise ratio than a Stark modulated spectrometer provided the double resonance waveguide cell is at least several times longer than the Stark cell.
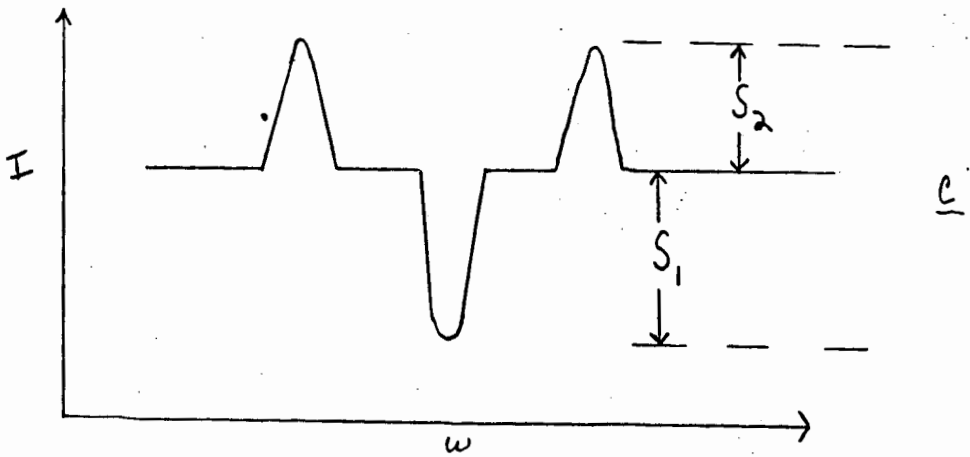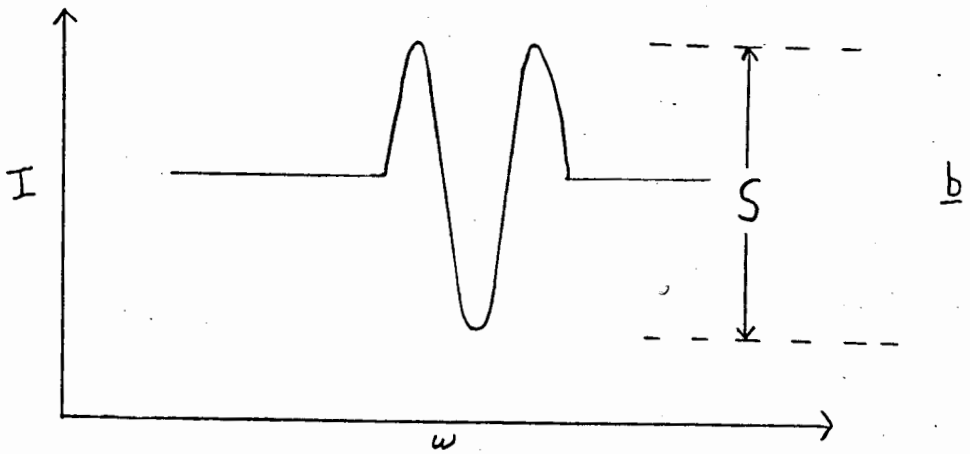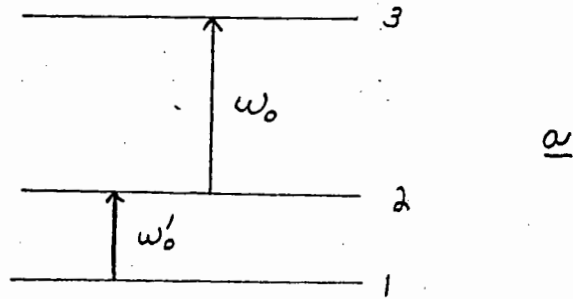
2. At high pressures, due to incomplete modulation, the double resonance technique is less advantageous than the Stark technique.

3. The double resonance technique is extremely useful for identification of molecules in a mixed sample due to the highly selective nature of the double resonance phenomenon.

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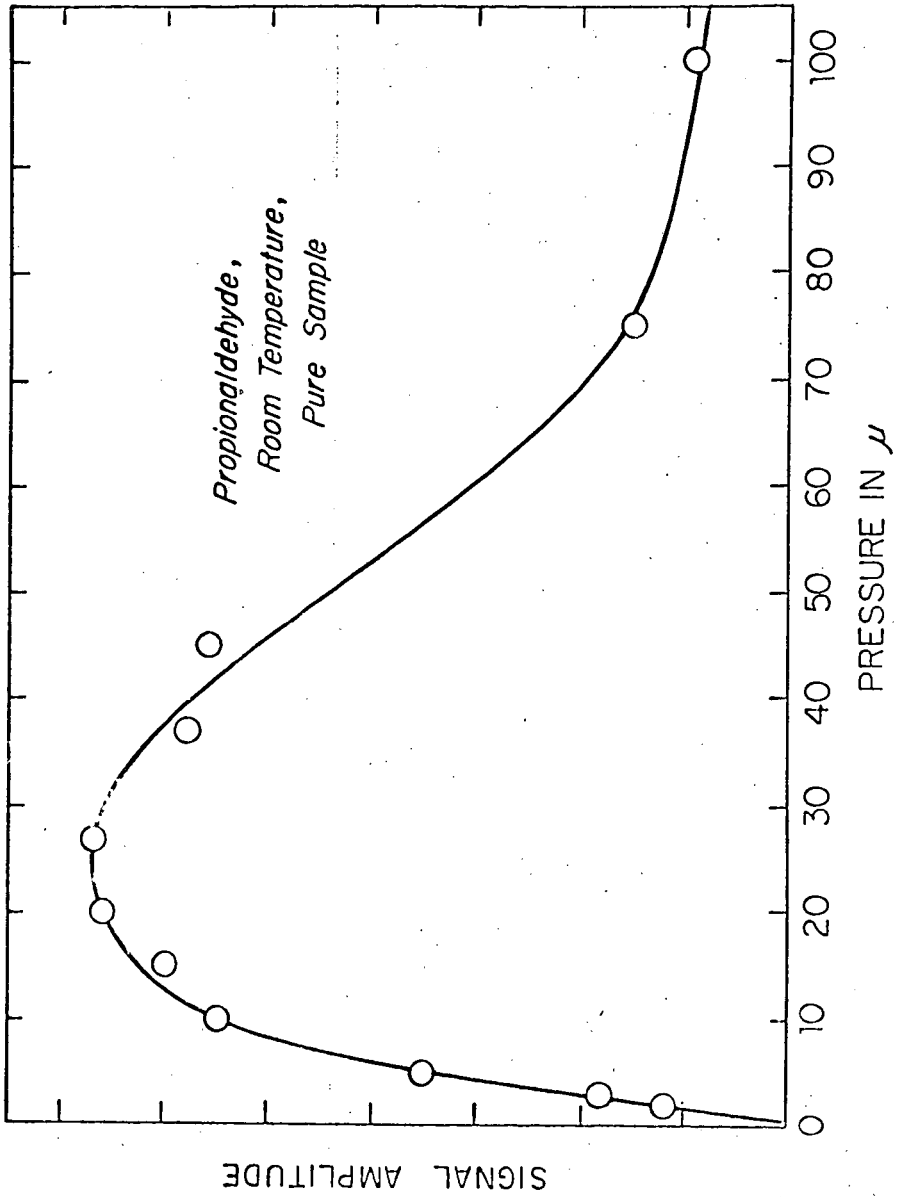10. Molecular Microwave Spectra Tables, NBS Circular 518.

Figure 1.

Propionaldehyde,
Room Temperature,
Pure Sample

SIGNAL AMPLITUDE

PRESSURE IN μ

Figure 2.